Improved Catalysts for Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Hosts

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Outline of Presentation

- Research objectives and background
- Research progress on the synthesis of zeolite Y nanoparticles
- Research progress on the synthesis of nanoporous hosts
- Summary
- Future plans for synthesis of nanocomposite catalysts and catalysts testing
- Acknowledgements

Research Objective

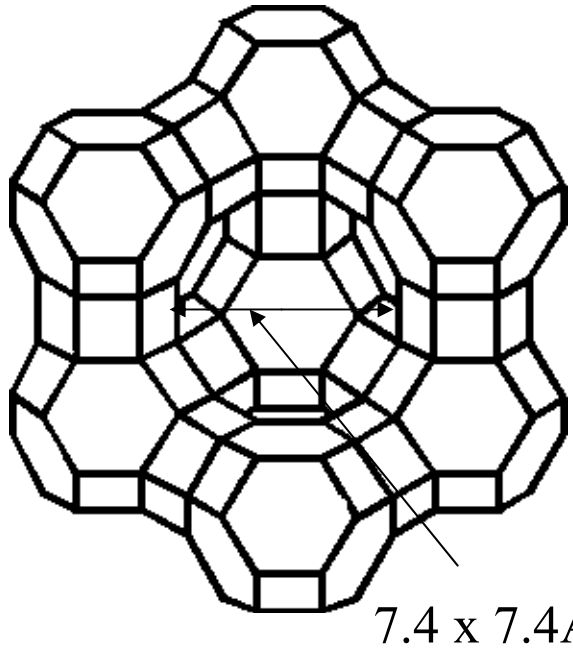
To synthesize a composite catalysts system (comprised of **Zeolite Y** nanoparticles encapsulated in stable nanoporous hosts) that is useful for heavy oil upgrading.

Motivation

Increasing demand for stable, resistant and very active catalysts for the conversion of heavy petroleum feedstock and residue to useful fuels (naptha and middle distillates).

Zeolite Y as Petroleum Catalyst

- Porous aluminosilicates with SiO_2 and AlO_2tetrahedra
- Si/Al ratio of zeolite ~ 2.5



- Synthetic counterpart to natural faujasite
- Extensively used as a component FCC process in the petroleum industry (Steam stabilized version-USY with Si/Al= 9)
- Typical particle is in micron size range
- **Limitation as catalyst**:
  - catalyst deactivation

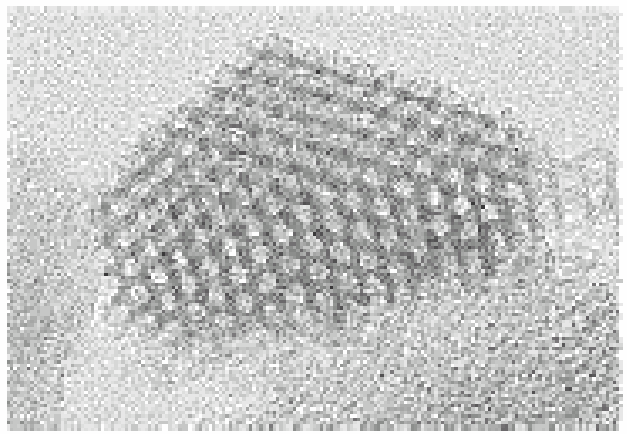
Advantages of Zeolite Y Nanoparticles over Conventional Micron-Size Zeolite Y

- Reduced diffusion path length, hence hydrocarbon substrates will diffuse in, are converted and the products quickly diffused out.

- Reduced over-reaction and hence reduced pore blockage and active sites deactivation.

Our Research Approach

- Synthesis of aluminosilicate nanoporous materials with pore diameter up to 30 nm (300 Å).



- Synthesis of zeolite Y nanoparticles (~30 nm) within the pores of the nanohosts.

- Testing the nanocomposite catalysts for the catalytic conversion of heavy petroleum substrates.

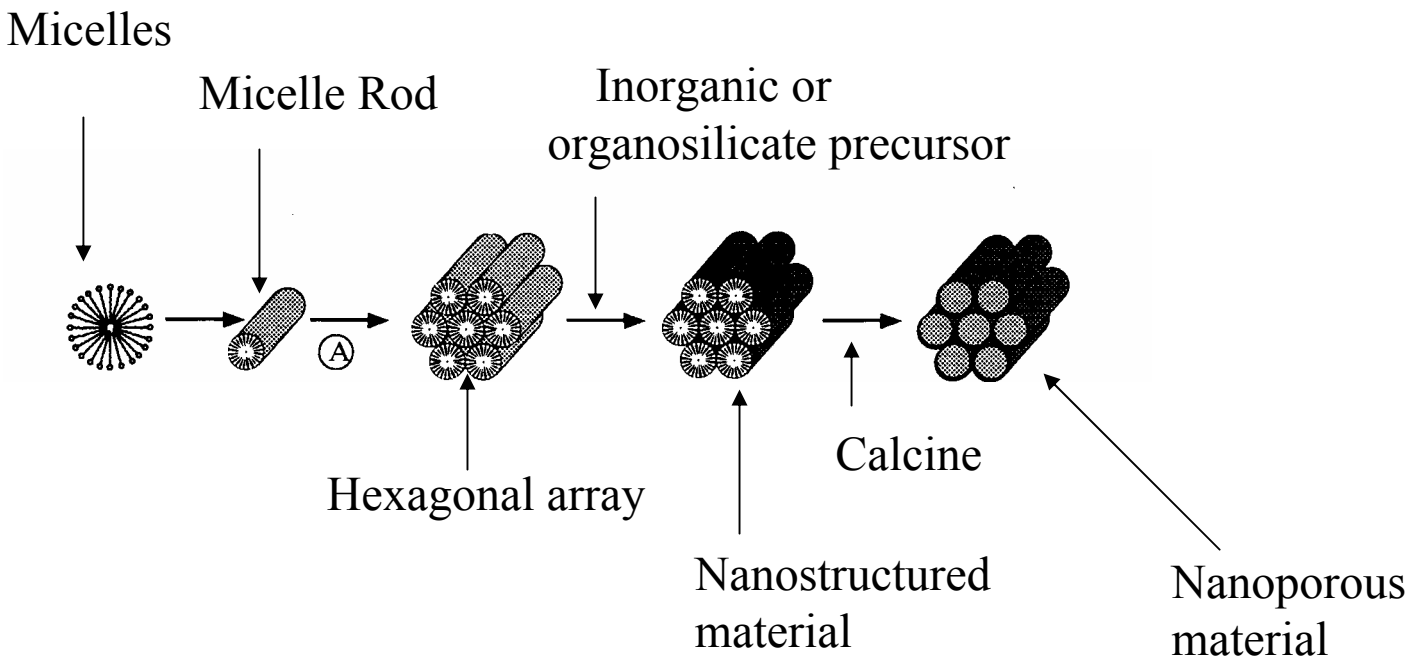
Role of the Nanoporous Host

- Perform as a mild hydrocracking catalyst for the initial conversion of bulky heavy oil substrates.

- Screen bulky hydrocarbon substrates from blocking the entrance to the zeolite pores, (reduce the extent of non selective, undesirable reactions on the external surfaces of the zeolite nanocrystals).

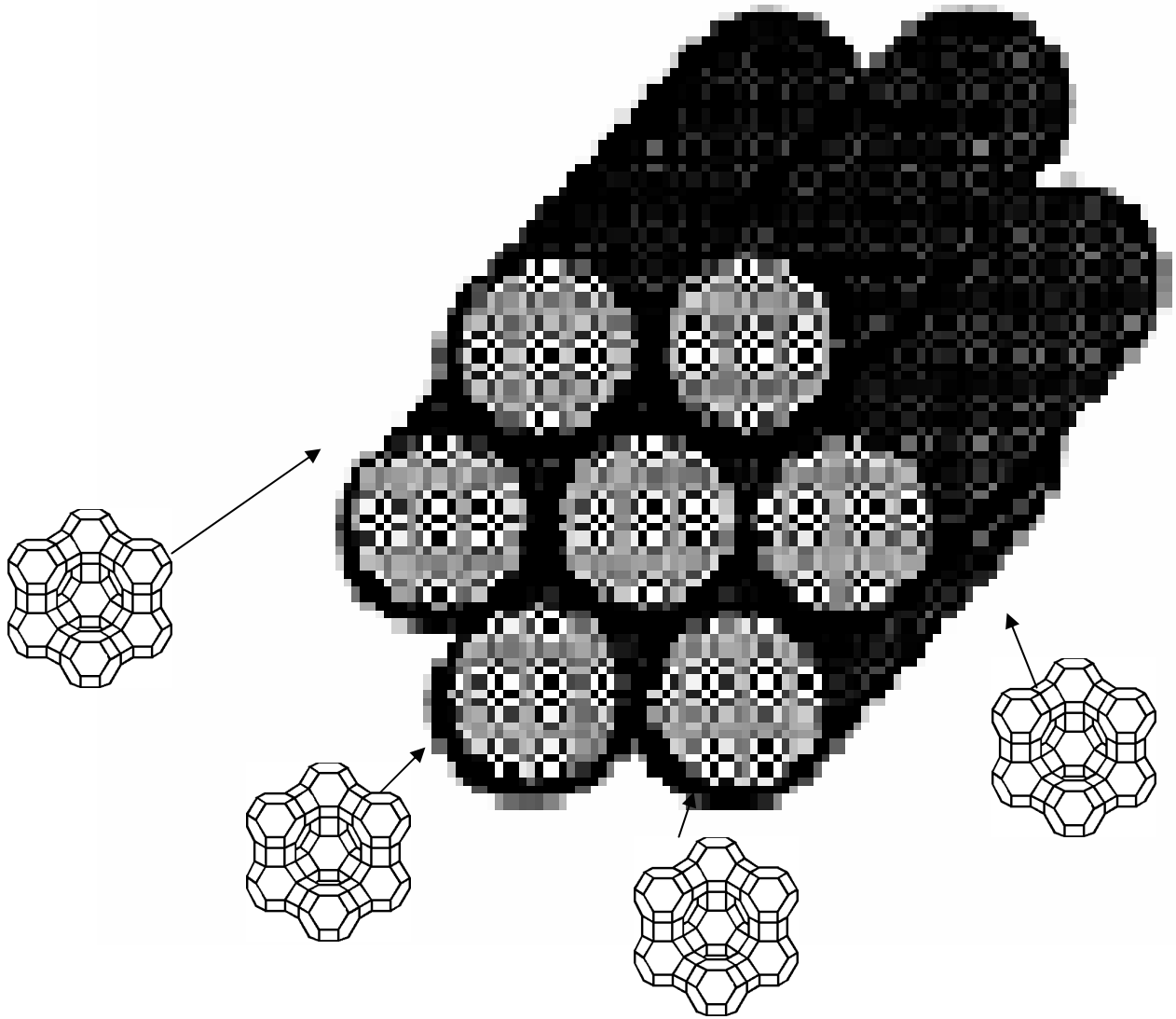
Synthesis of Nanoporous Silicate

Surfactant templating mechanism



J. S. Beck, J. C. Vartuli, W. J. Roth, M .E. Leonowicz, C. T. Kresge, K. D. Schmitt, C-TW Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, JACS 114 270 (1992) 10834-43.

Inserting Zeolite Y Nanoparticles Through Direct Synthesis



Progress on Zeolite Y Synthesis

Standard Zeolite Y synthesis:

- sodium hydroxide (NaOH)
- sodium aluminate ($NaAlO_2$)
- sodium silicate
- High shear mixing conditions, 24 h at RT and 22 h at 100ºC.
  (molar composition: $4.62Na_2O:Al_2O_3:SiO_2:180\ H_2O$)

(Verified Synthesis Recipe for Zeolites, H. Robson, 1997)

Nanoparticles Zeolite Y Synthesis :

Method 1

- sodium chloride
- aluminum isopropoxide- $[(CH_3)_2CHO]_3Al$
- tetraethylorthosilicate (TEOS) – $(C_2H_5O)_4Si$
- tetramethylammonium hydroxide (TMAOH)- $(C_2H_5)_4NOH$
- filter clear solution
- stir for 3 days RT, 4 days at 100ºC
- recover product by centrifuge at 15000 g for 40 minutes

Method 2

method 1 + with NaOH instead of NaCl

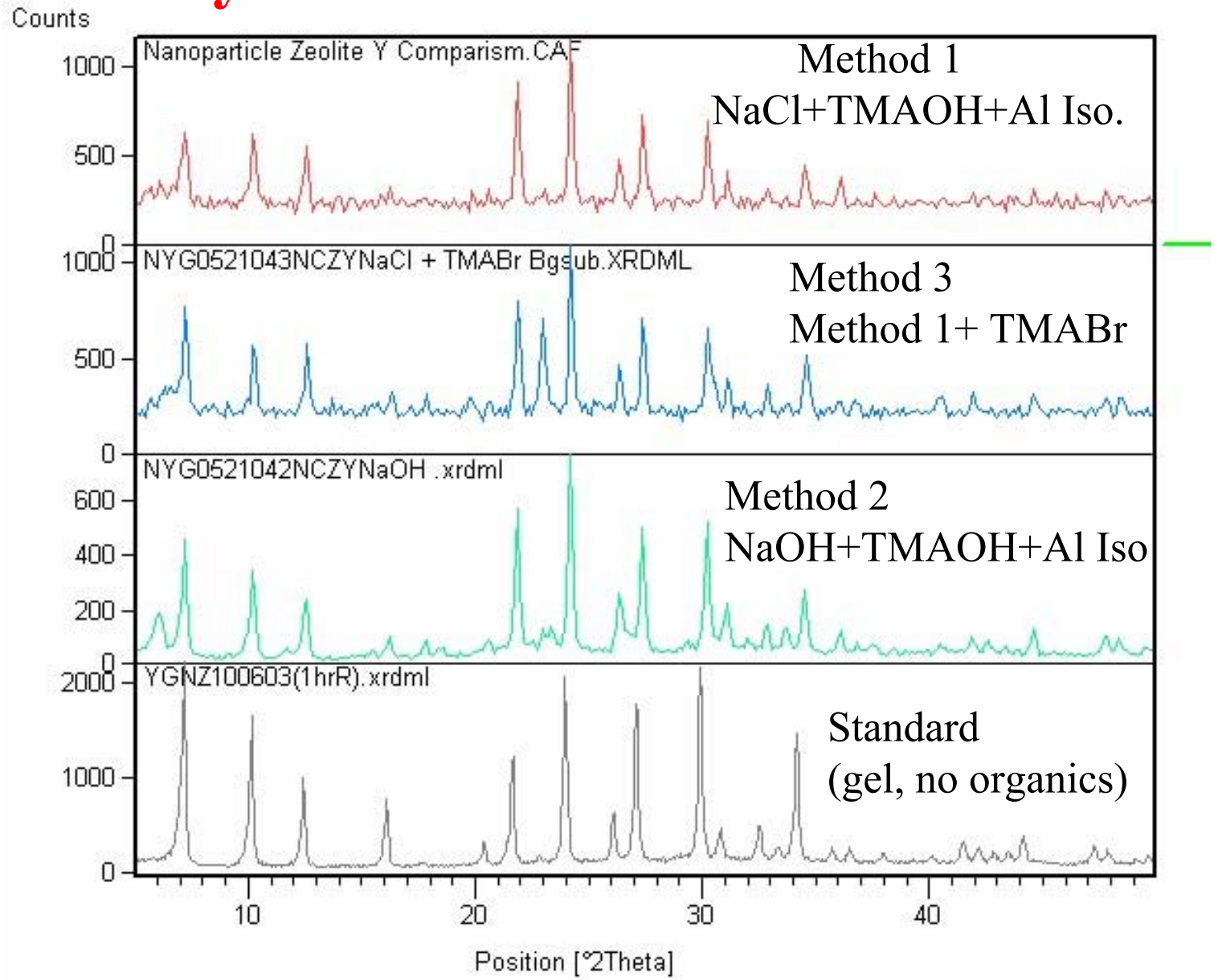
Method 3

method 1 + tetramethylammonium bromide (TMABr) - $(C_4H_{12}NBr)$

$(1Al_2O_3{:}4.36SiO_2{:}2.3TMAOH{:}0.6TMABr{:}0.048Na_2O)$

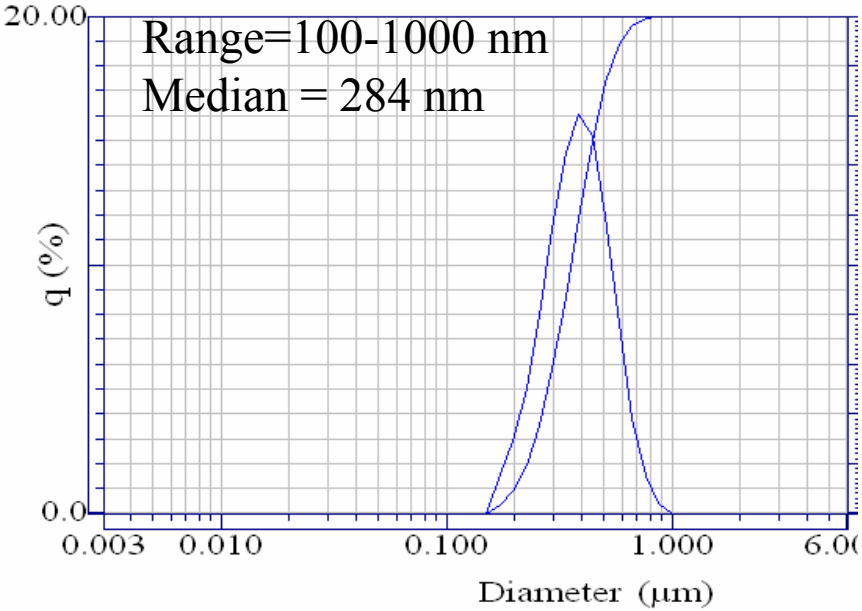
Yan et al., Microporous and Mesoporous materials, 2003

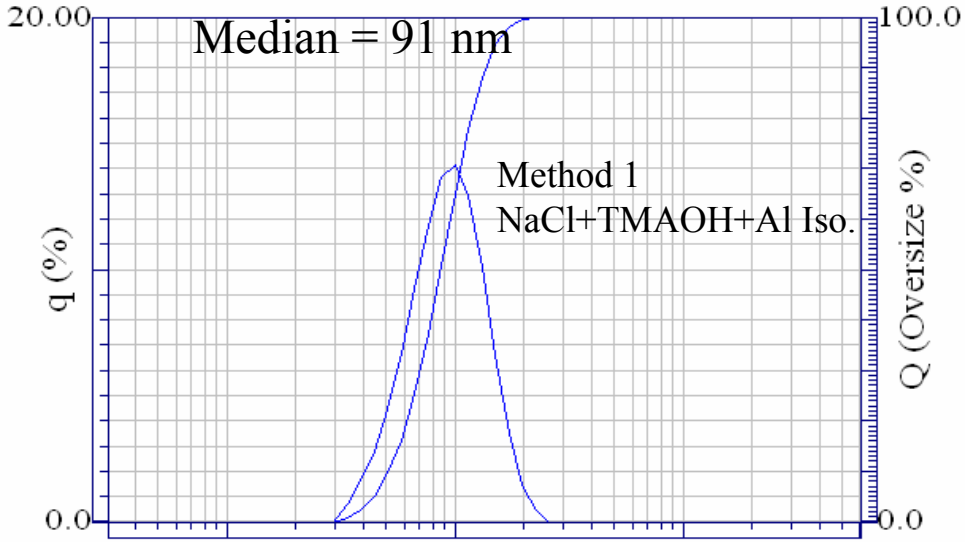
X-Ray Diffraction Patterns of Zeolite Y

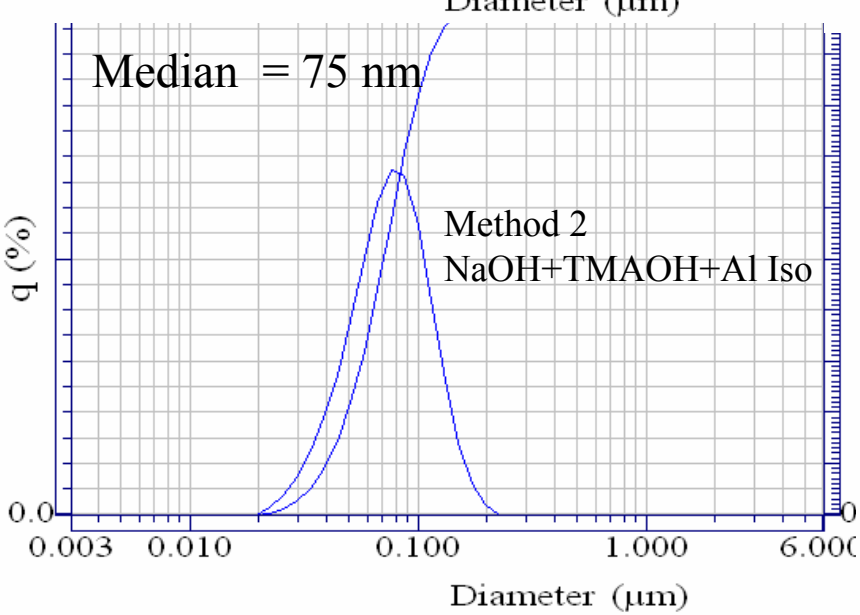


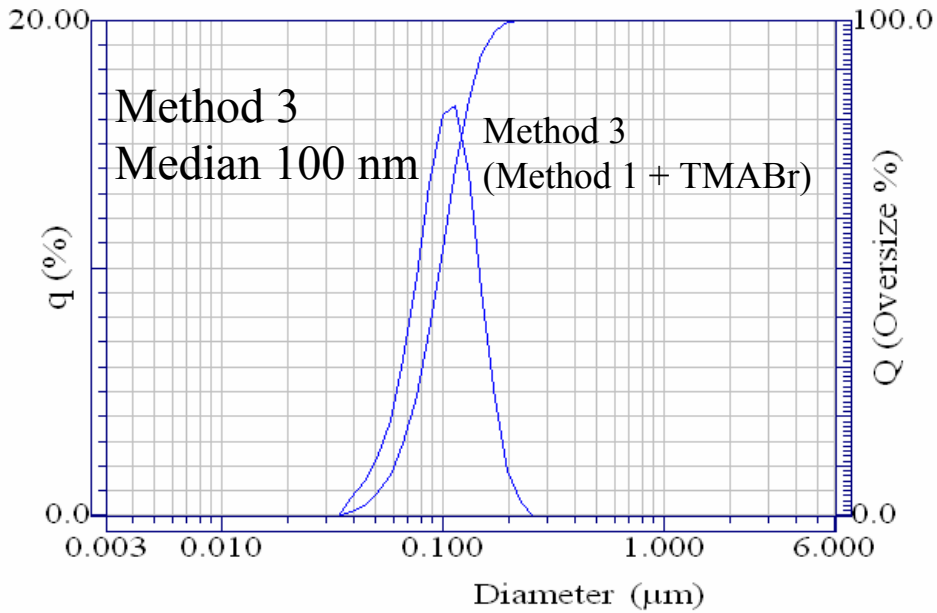
No crystals using Ludox AS-30, HS-30 as SiO_2

Dynamic Light Scattering Particle Size Analysis

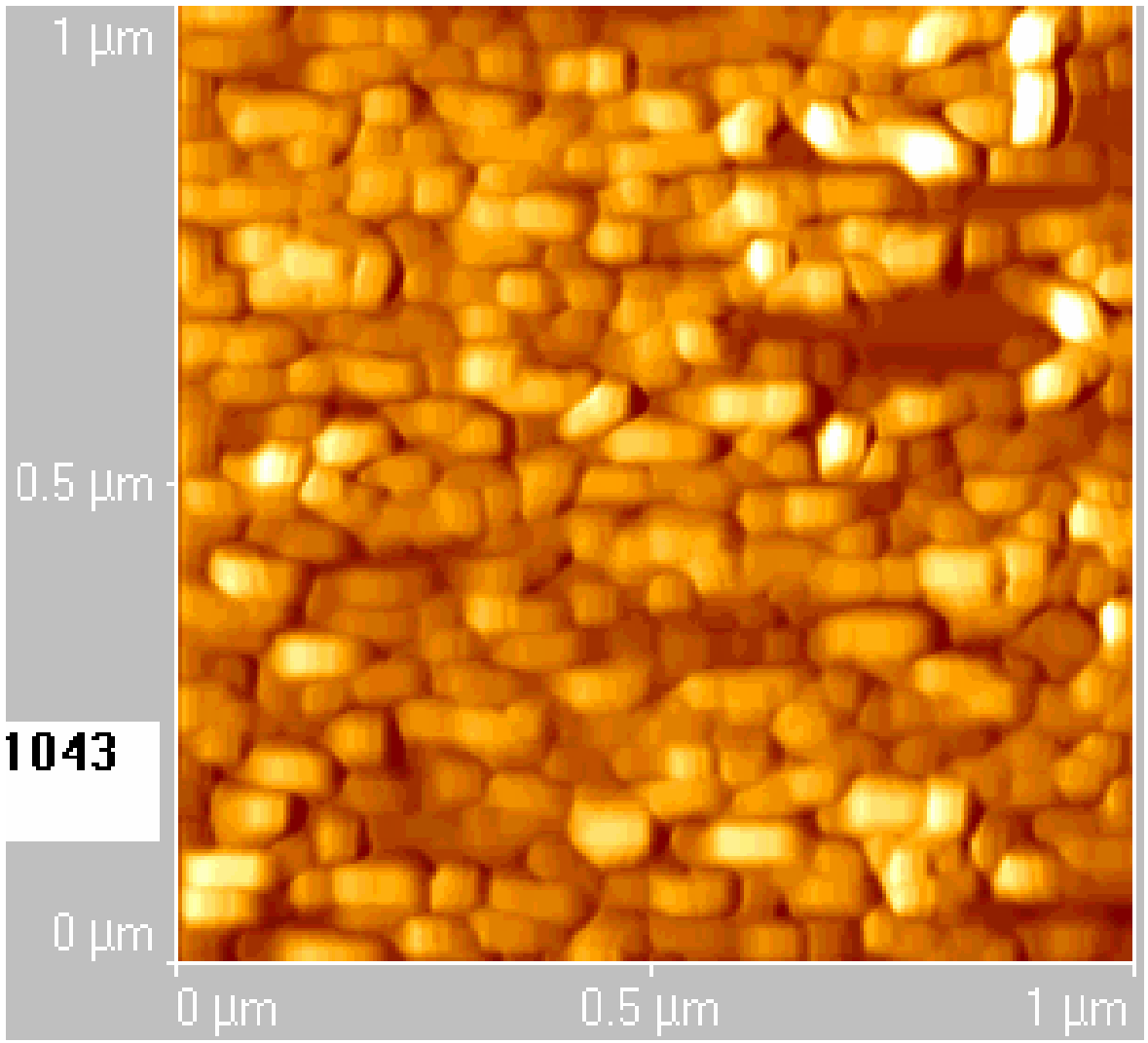








Atomic Force Microscope Image of Zeolite Nanoparticles from NaCl+TMAOH+ TMABr + Al Iso.



110 x 60 x 27 nm

Future Work on Zeollite Y syntheis

Continue to explore synthesis variables to reduce the size of the nanocrystals.

Progress on the Synthesis of Nanoporous Host

General synthesis approach

Precursor: (TEOS, Al Isopropoxide)

H+

$(C_{18}H_{35}(OCH_2CH_2)_{10}OH)$

40ºC, 24 hr, then 90ºC 24 hr.

Nanostructured Organosilicate

Extraction in EtOH/HCl

Nanoporous Organosilicate

Organic Templates Used

Nonionic Alkyl (polyethylene oxide) Surfactants

Brij $_{30}$	$C_{12}(EO)_4$
Brij $_{78}$	$C_{16}(EO)_{10}$
Brij $_{76}$	$C_{18}(EO)_{10}$

Nonionic Triblock Copolymers

Pluronic L-121	$EO_5PO_{70}EO_5$
Pluronic P-64	$EO_{13}PO_{30}EO_{13}$
Pluronic F-68	$EO_{80}PO_{30}EO_{80}$
Pluronic P-123	$EO_{20}PO_{70}EO_{20}$

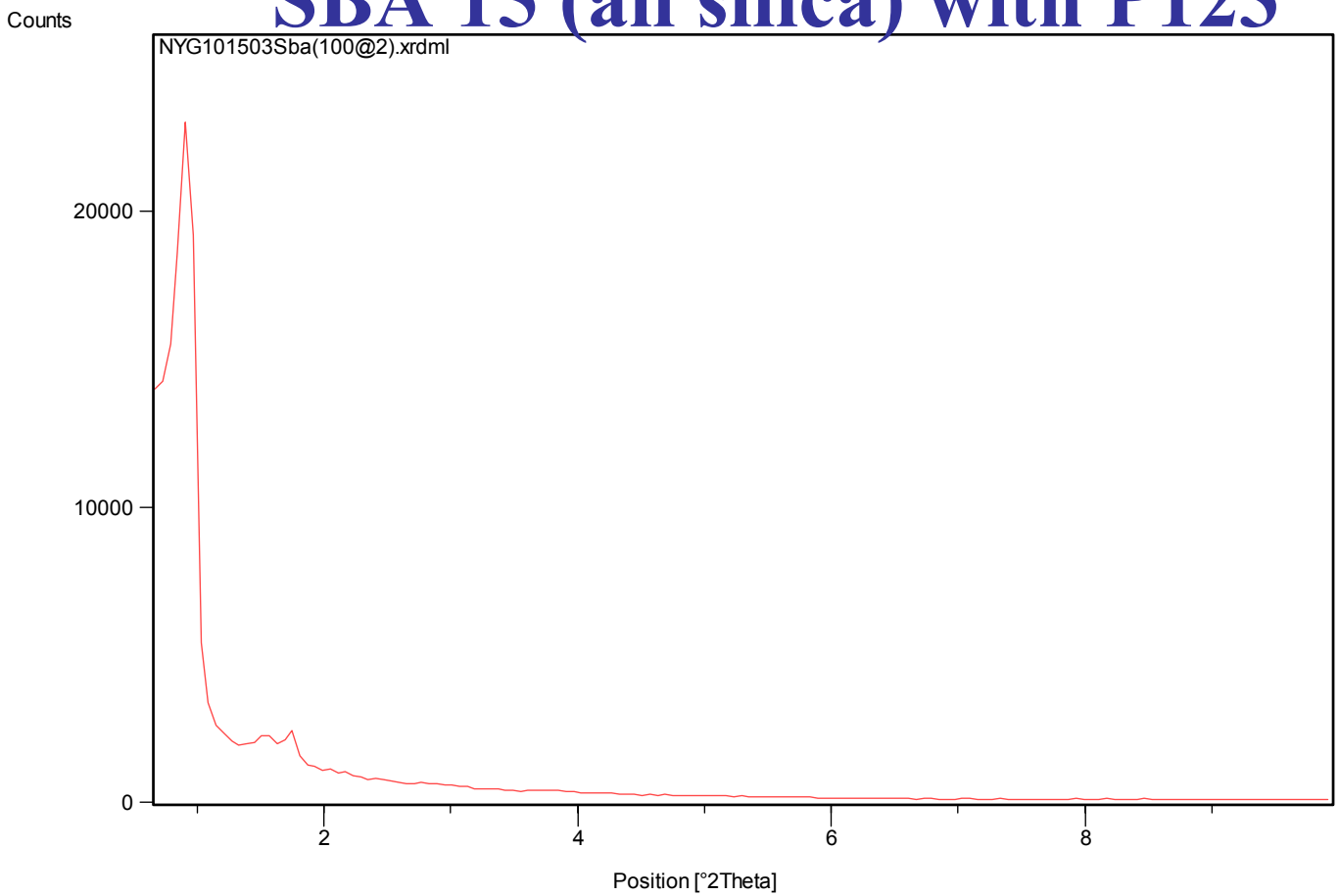
Cationic Surfactants

Cetyltrimethylammonium $CH_3(CH_2)_{15}N(CH_3)_3^+$

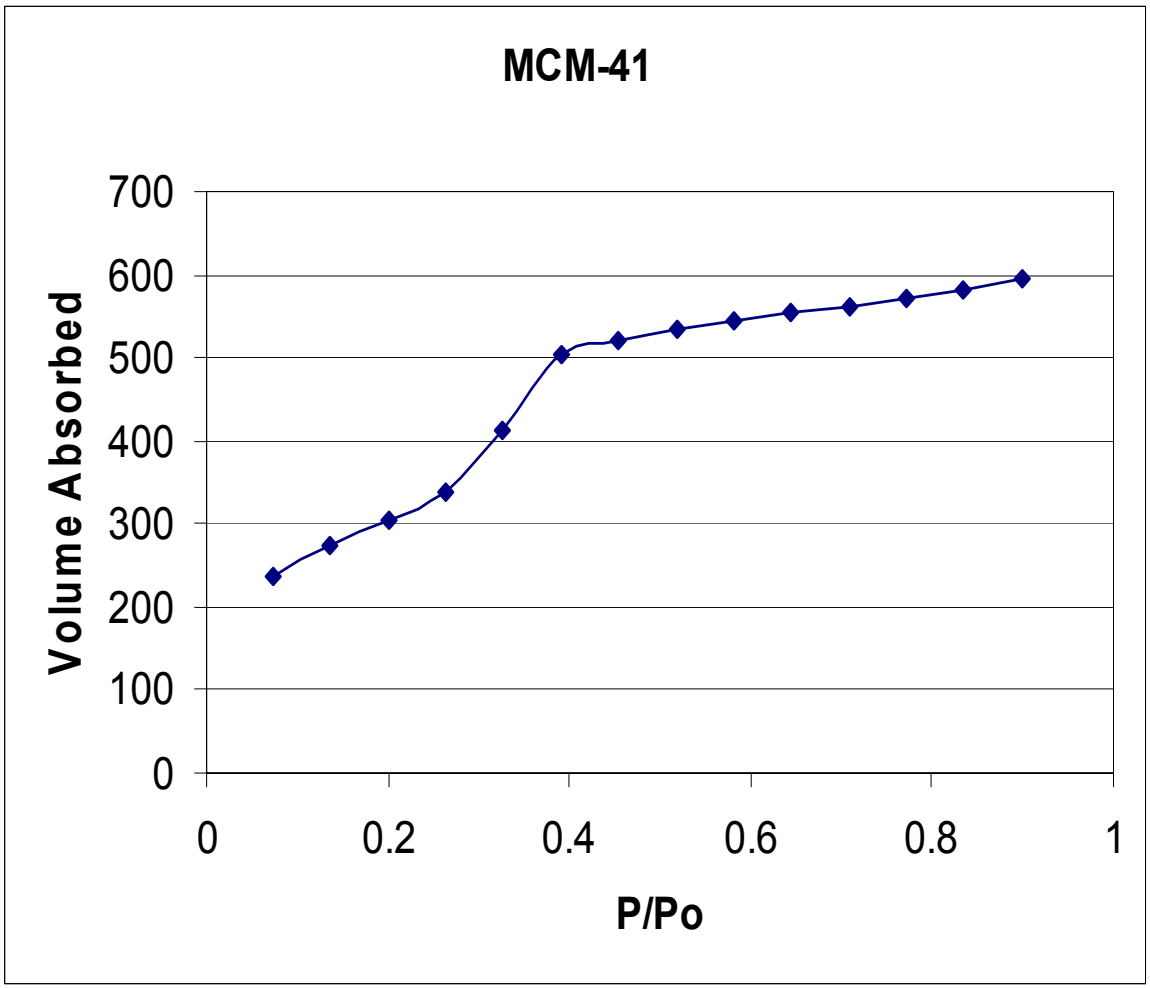
(EO = ethylene oxide units, PO = propylene oxide units)

Results for Synthesis of All Silica/Aluminosilicate Nanoporous Host

X-Ray Diffraction Pattern of Nanoporous SBA 15 (all silica) with P123



Nitrogen Adsorption Isotherm of Nanoporous SBA 15

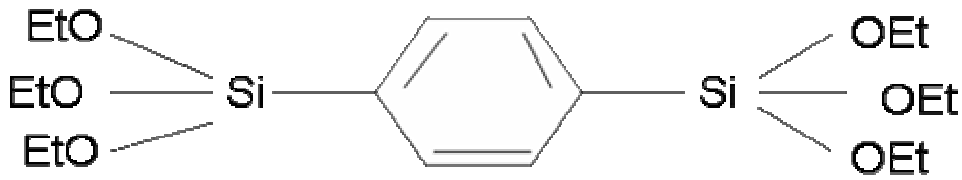


Pore size 4 nm (40 Å)

Surface area : 980 m^2/g

Synthesis of Organosilicate Nanoporous Host (Acid condition and nonionic surfactant)

Precursor: 1,4 bis-triethoxysily benzene (BTEB)



H+

$(C_{18}H_{35}(OCH_2CH_2)_{10}OH)$

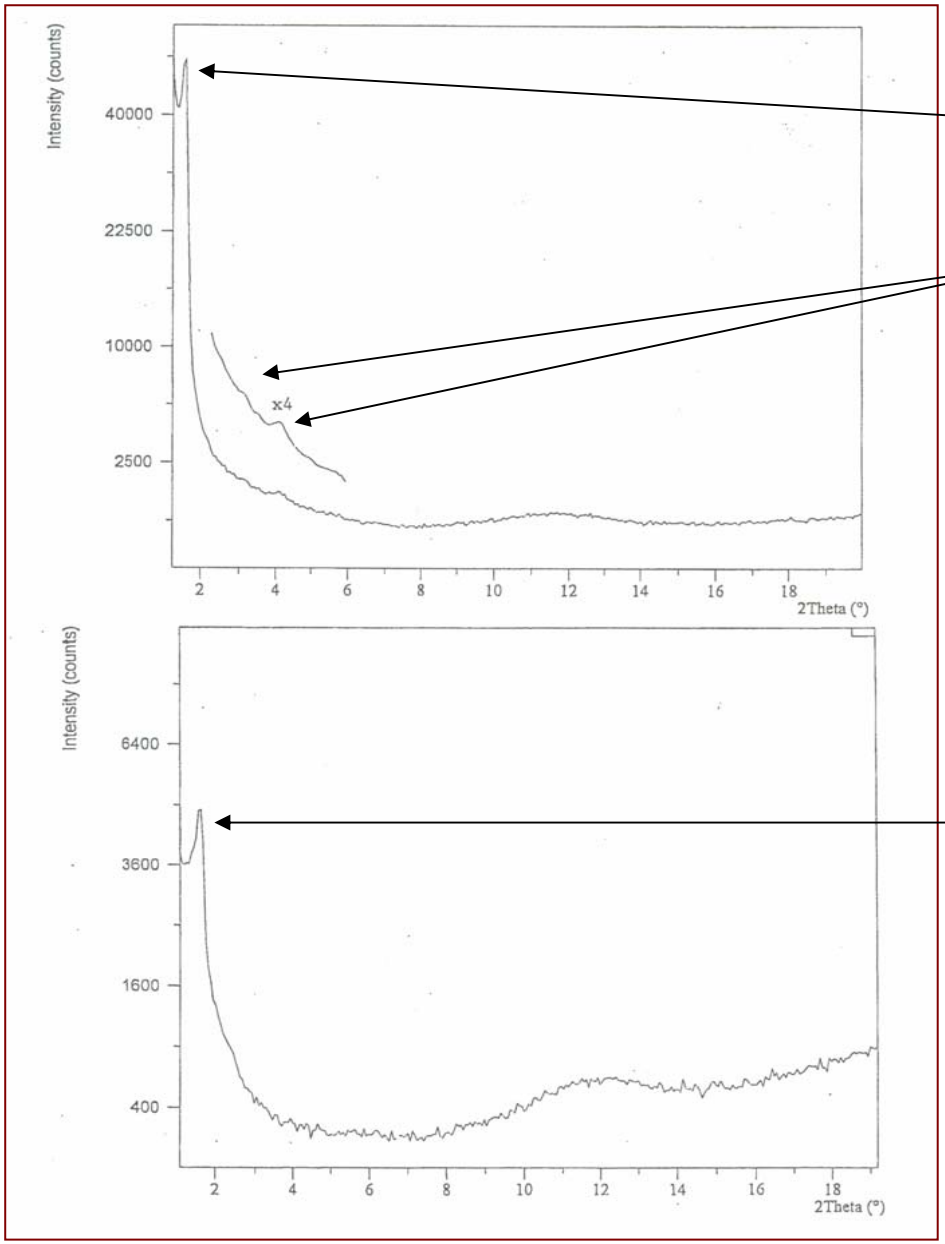
40ºC, 24 hr, then 90ºC 24 hr.

Nanostructured Organosilicate

Extraction in EtOH/HCl

Nanoporous Organosilicate

X-Ray Diffraction Patterns



Extracted Organosilicate

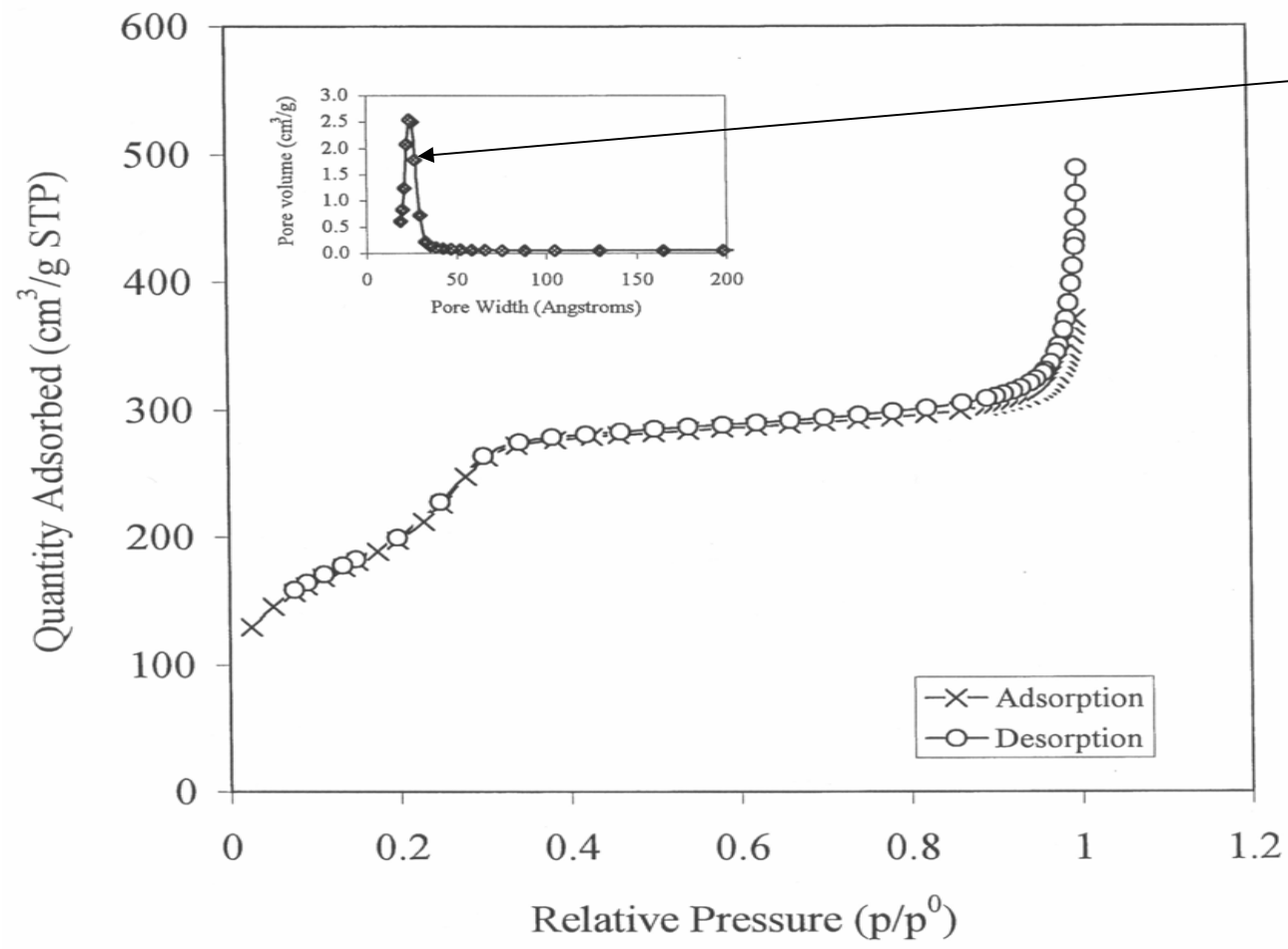
2θ =1.6° (d = 55.3 Å)

2θ = 3.3° & 4.1°
(d =27.1 Å & 21.4 Å)

"As Synthesized" organosilicate

2θ =1.6° (d = 55.3 Å)

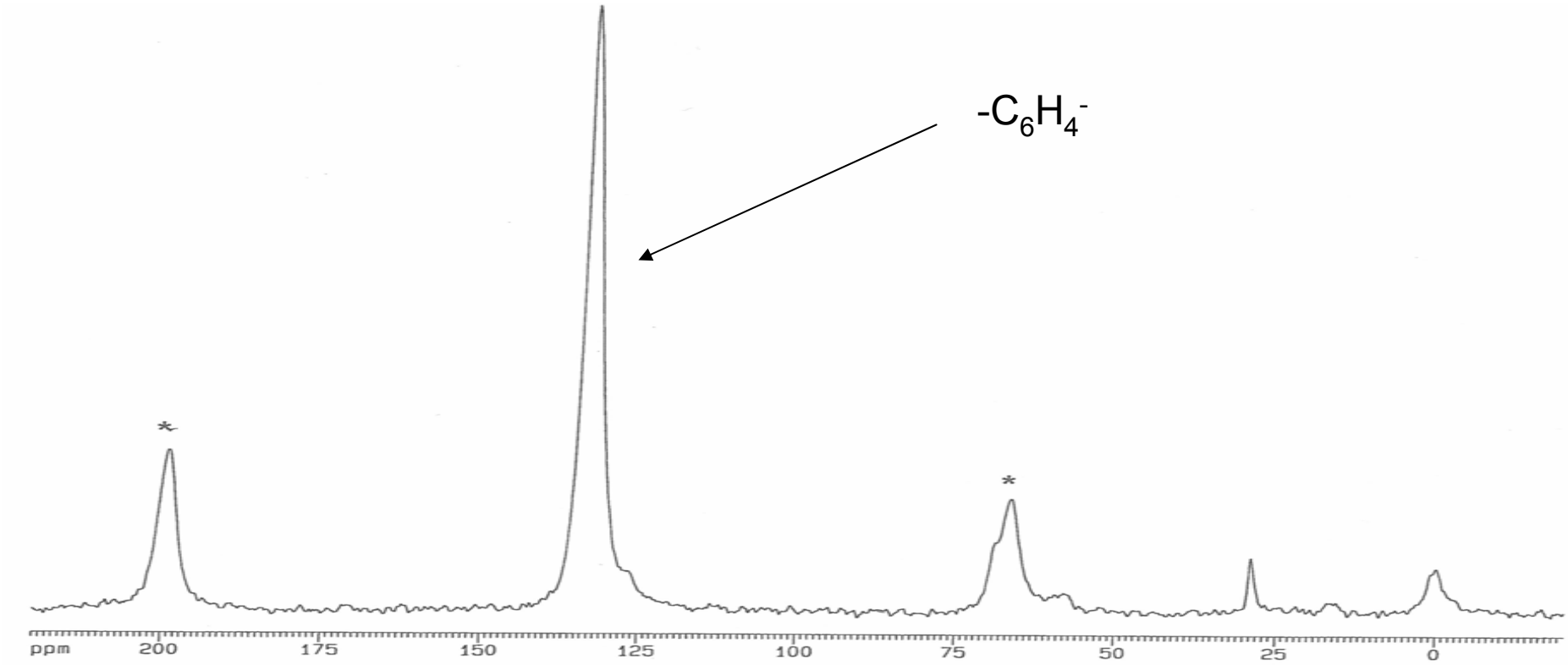
Nitrogen Adsorption-Desorption Isotherms



- Pore diameter 27.4Å
- Surface area 784 m^{2}/g

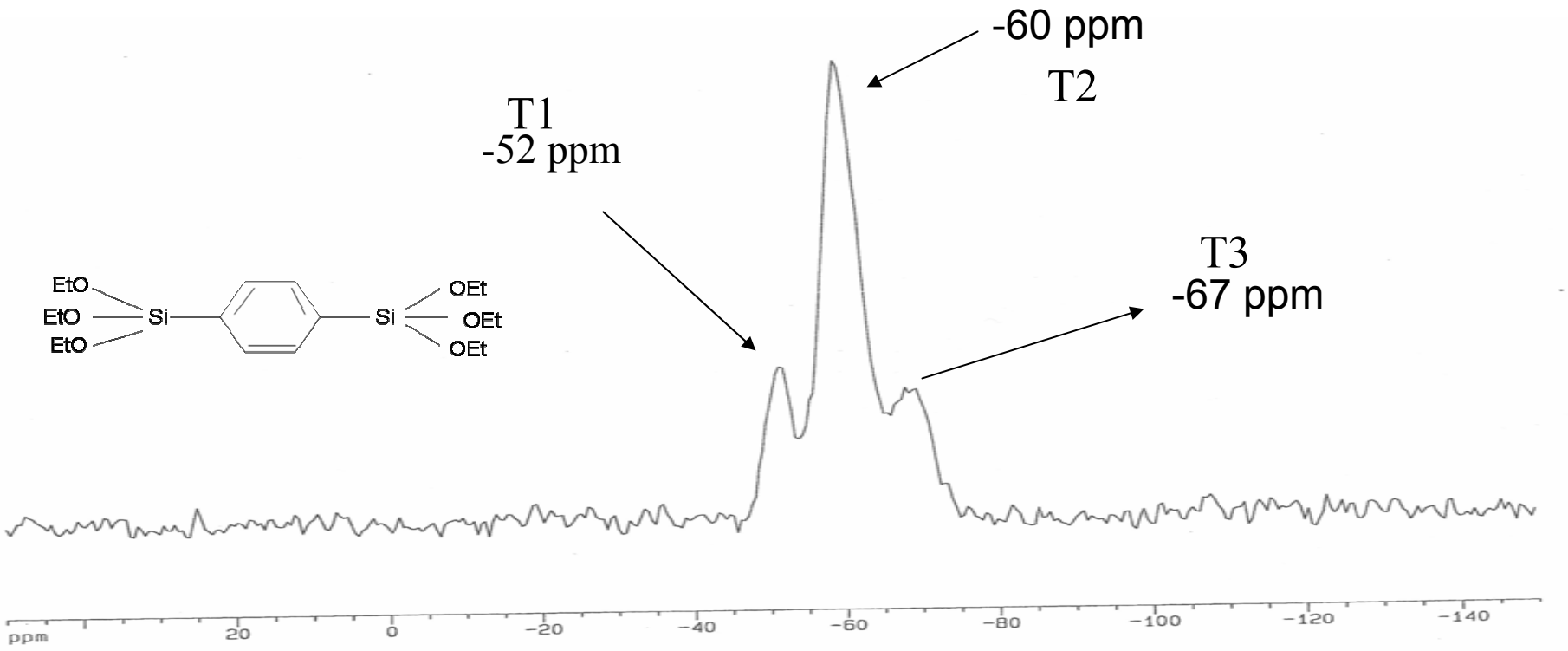
Isotherms acquired on a Micromeretics ASAP 2010 Porosimeter

^{13}C Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample



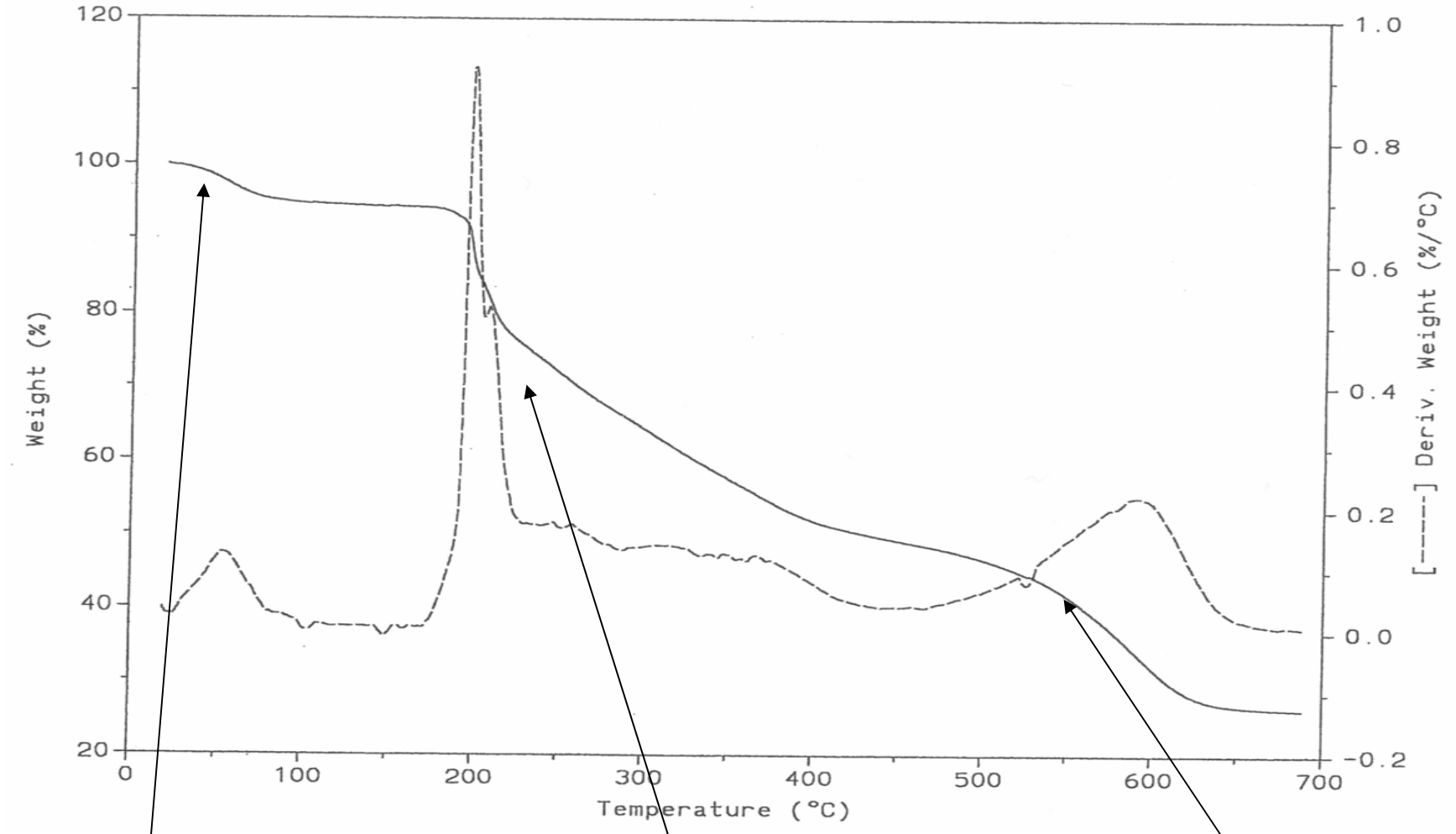
This shows that Si-C bond remained in-tact in the product.

^{29}Si Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample



67 % condensation of the organosilicate precursor was observed.

Weight-Loss Thermogram of "As-synthesized" Phenylene-bridged Organosilicate

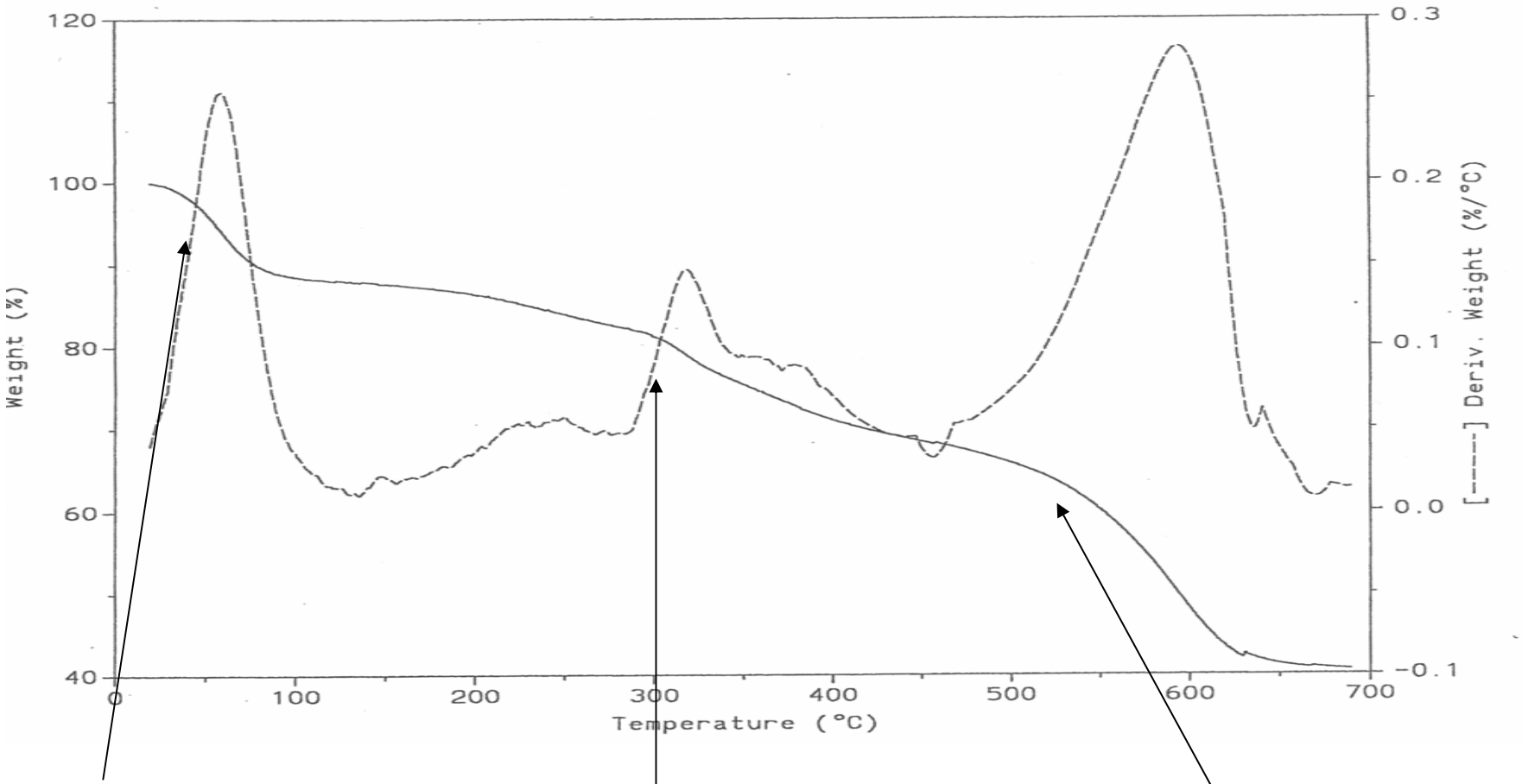


EtOH and H_2O = 8%

Surfactant = 45%

$-C_6H_4-$

Weight-Loss Thermogram of "Ethanol/HCl Extracted" Phenylene-bridged Organosilicate

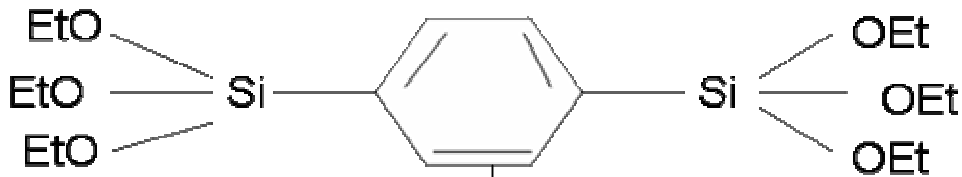


$H_2O = 8\%$

Residual surfactant = 8%

$-C_6H_4-$

Synthesis of Organosilicate Nanoporous Host (Base condition & cationic template)



OH^-

(Cetryltrimethylammonium Bromide)

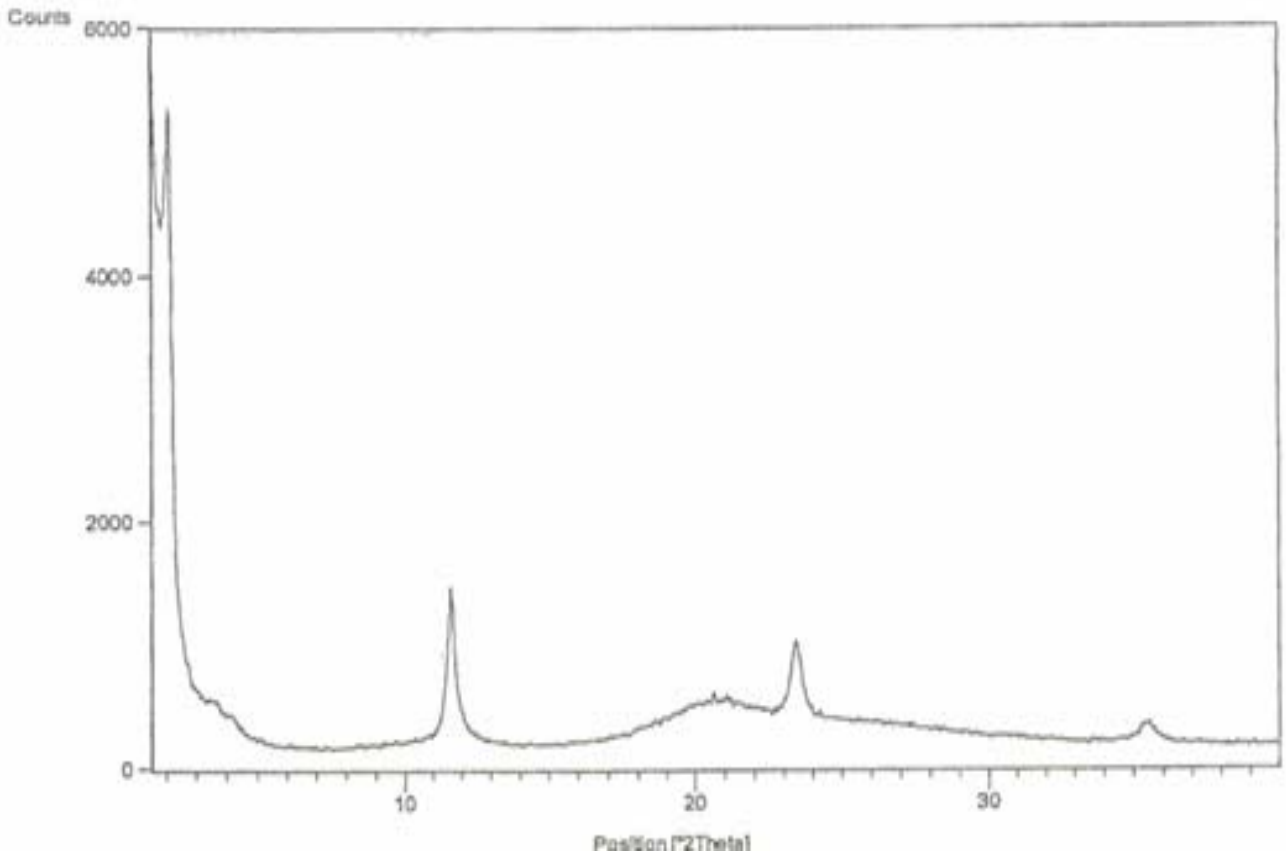
40ºC, 24 hr, then 90ºC 24 hr.

Nanostructured Organosilicate

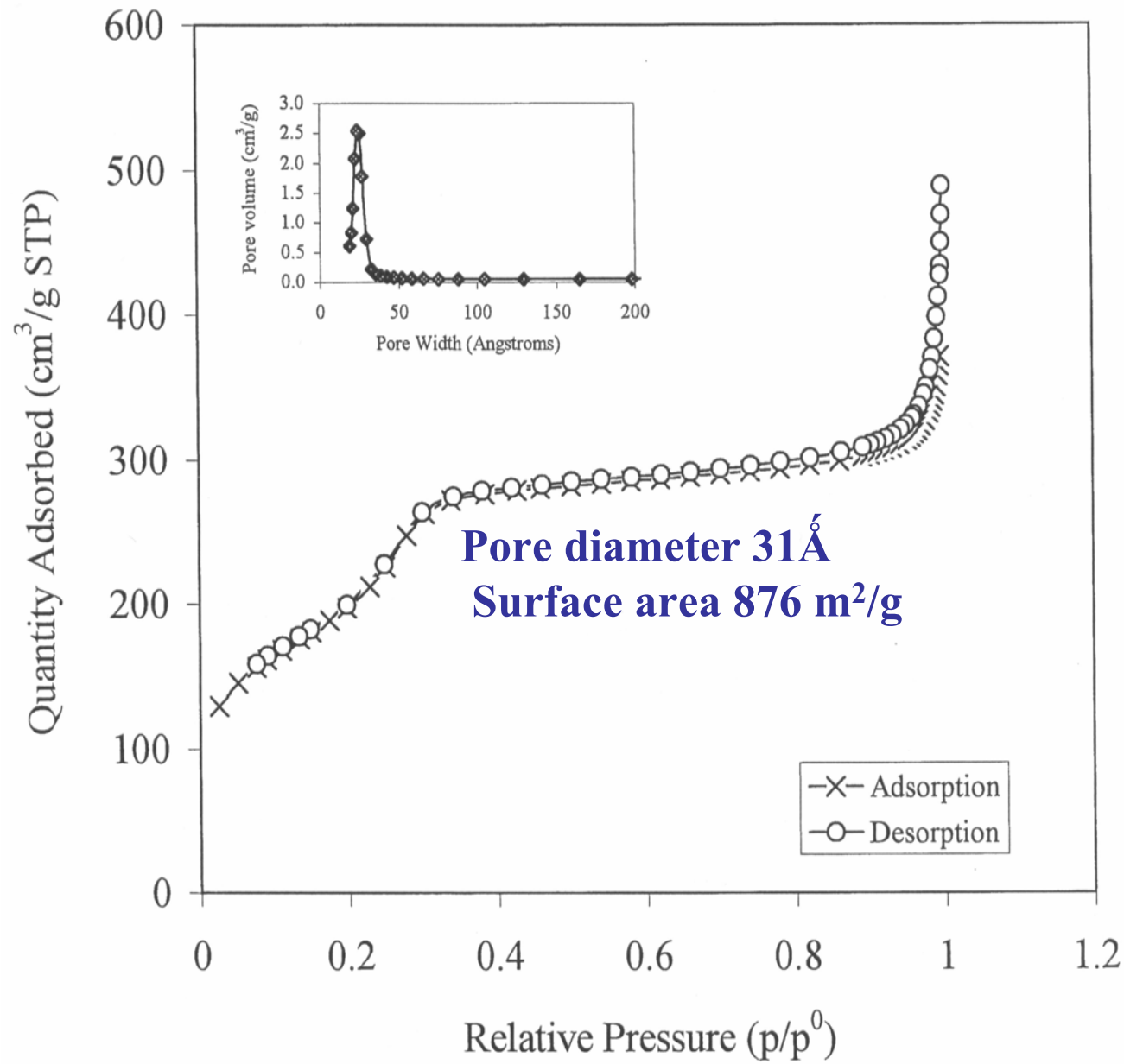
Extraction in EtOH/HCl

Nanoporous Organosilicate

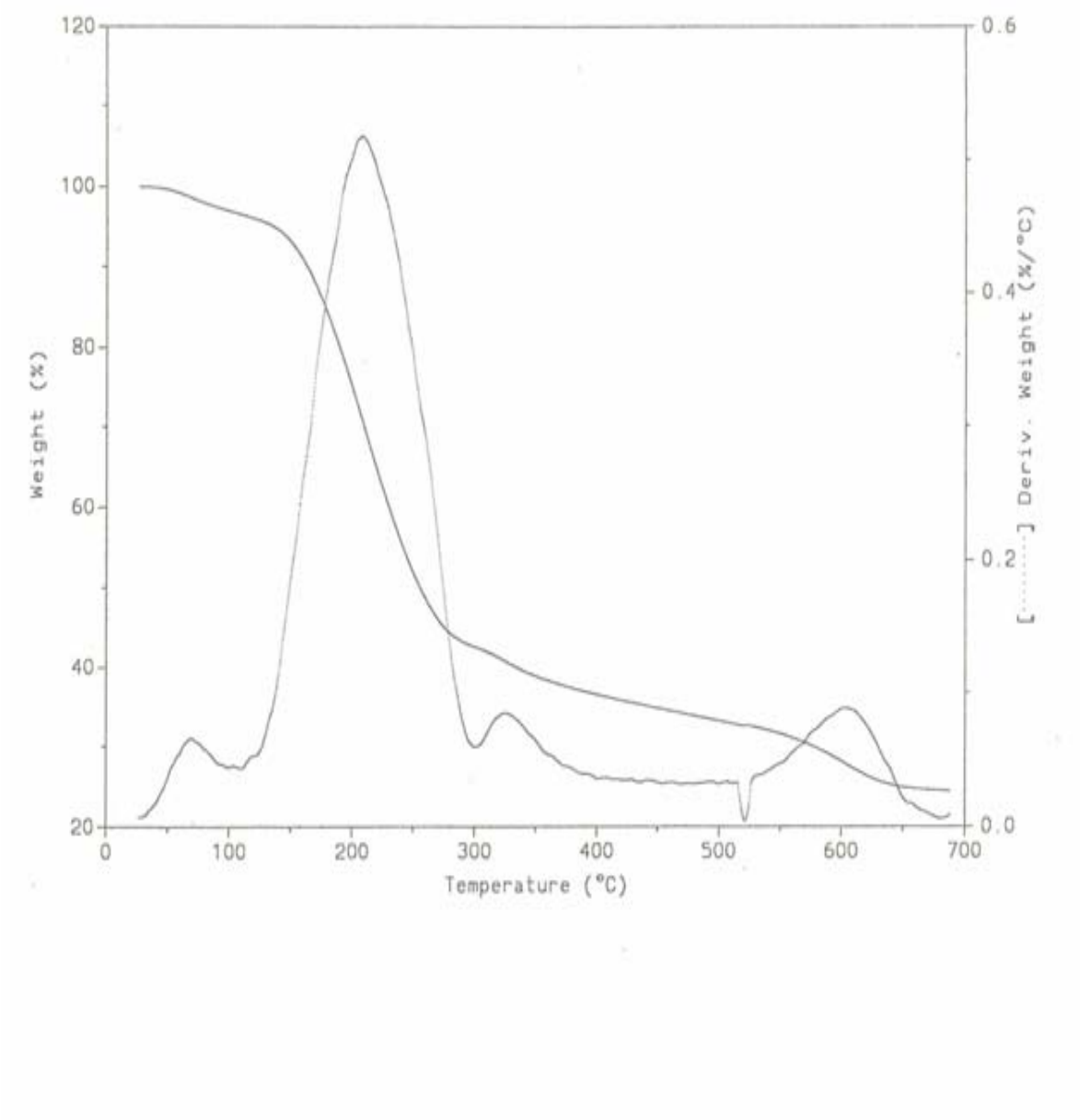
X-Ray Diffraction



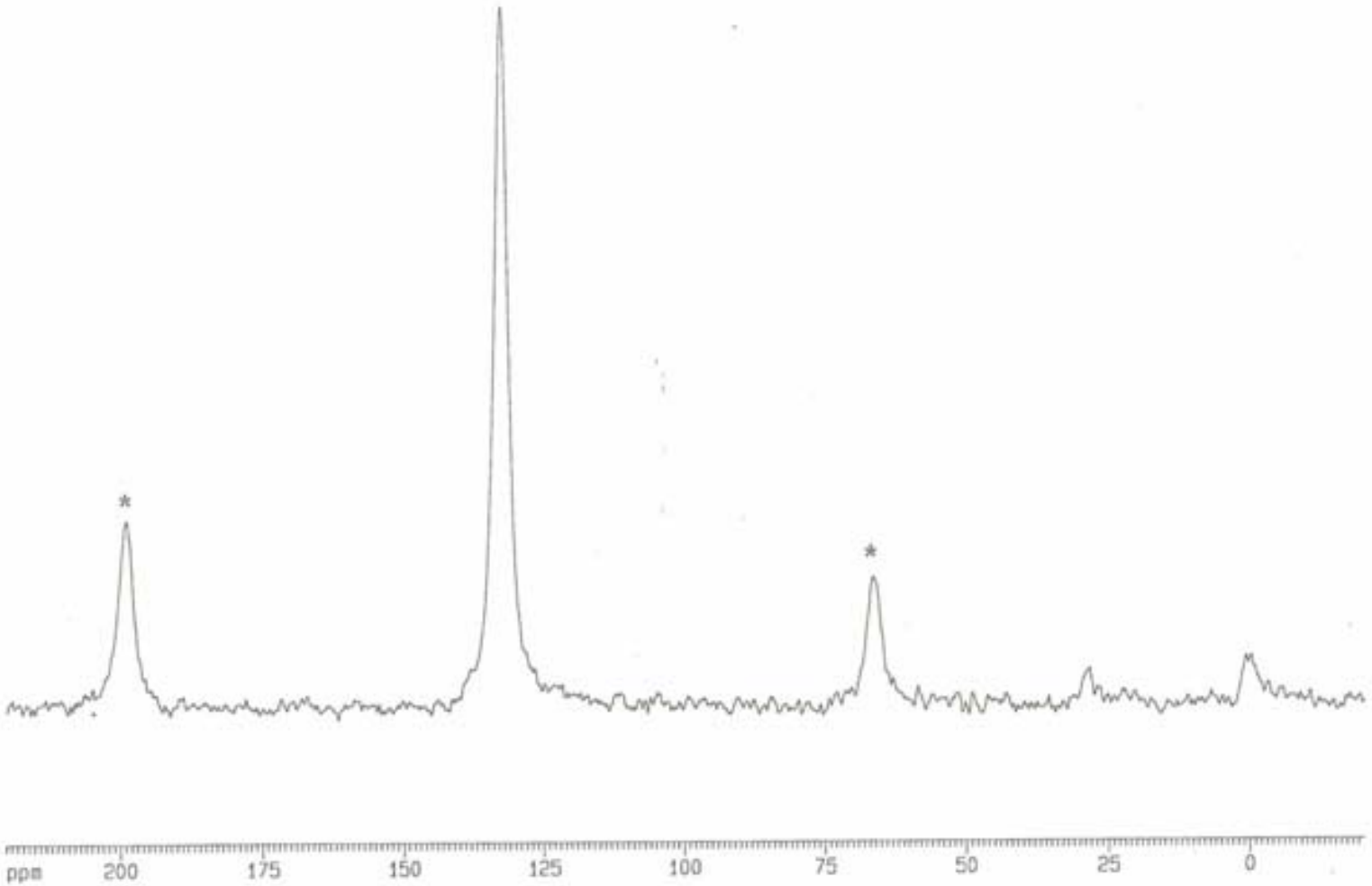
Adsorption/Desorption Isotherm



Weight-Loss Thermogram of "As-synthesized" Phenylene-bridged Organosilicate

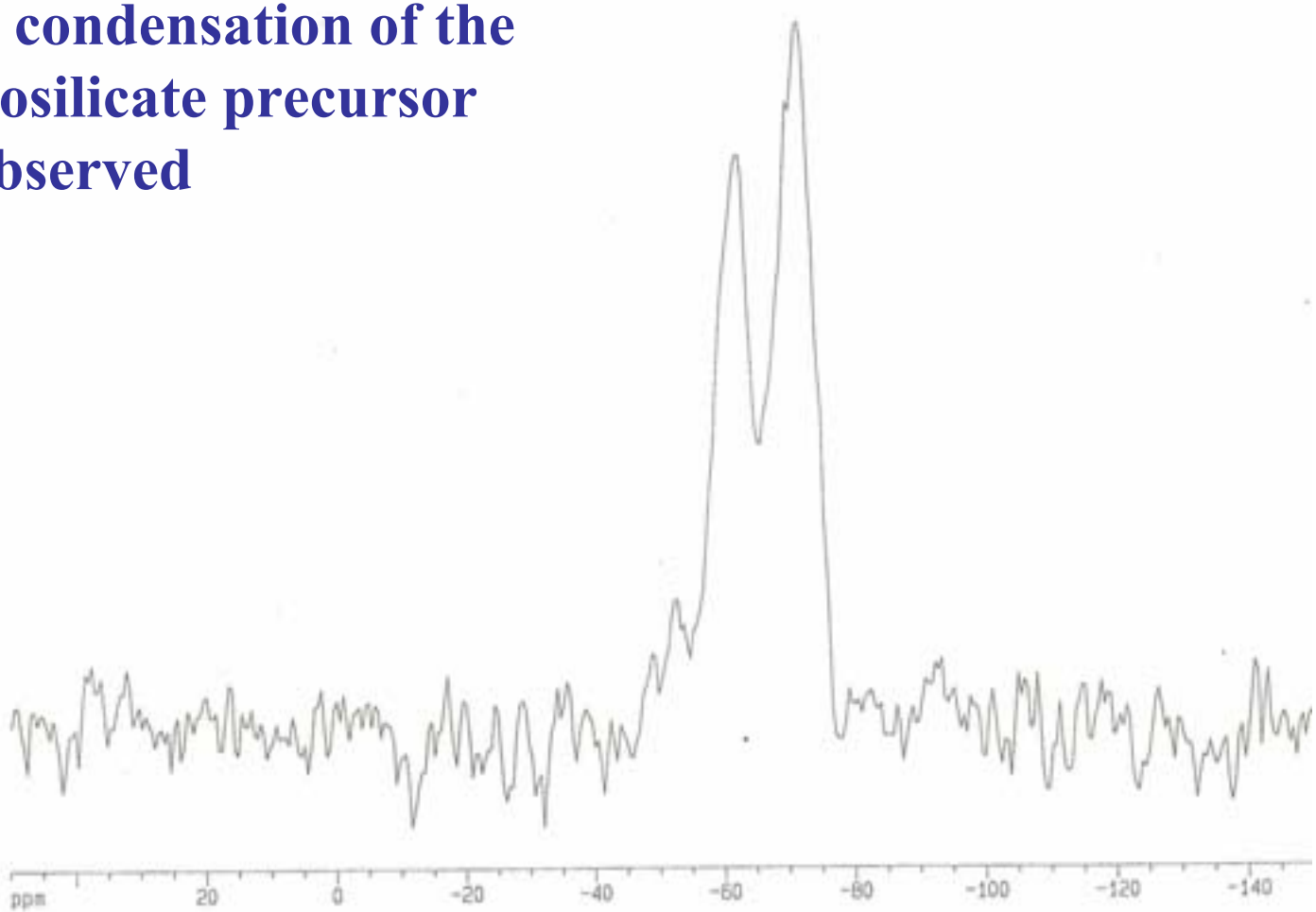


^{13}C Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample

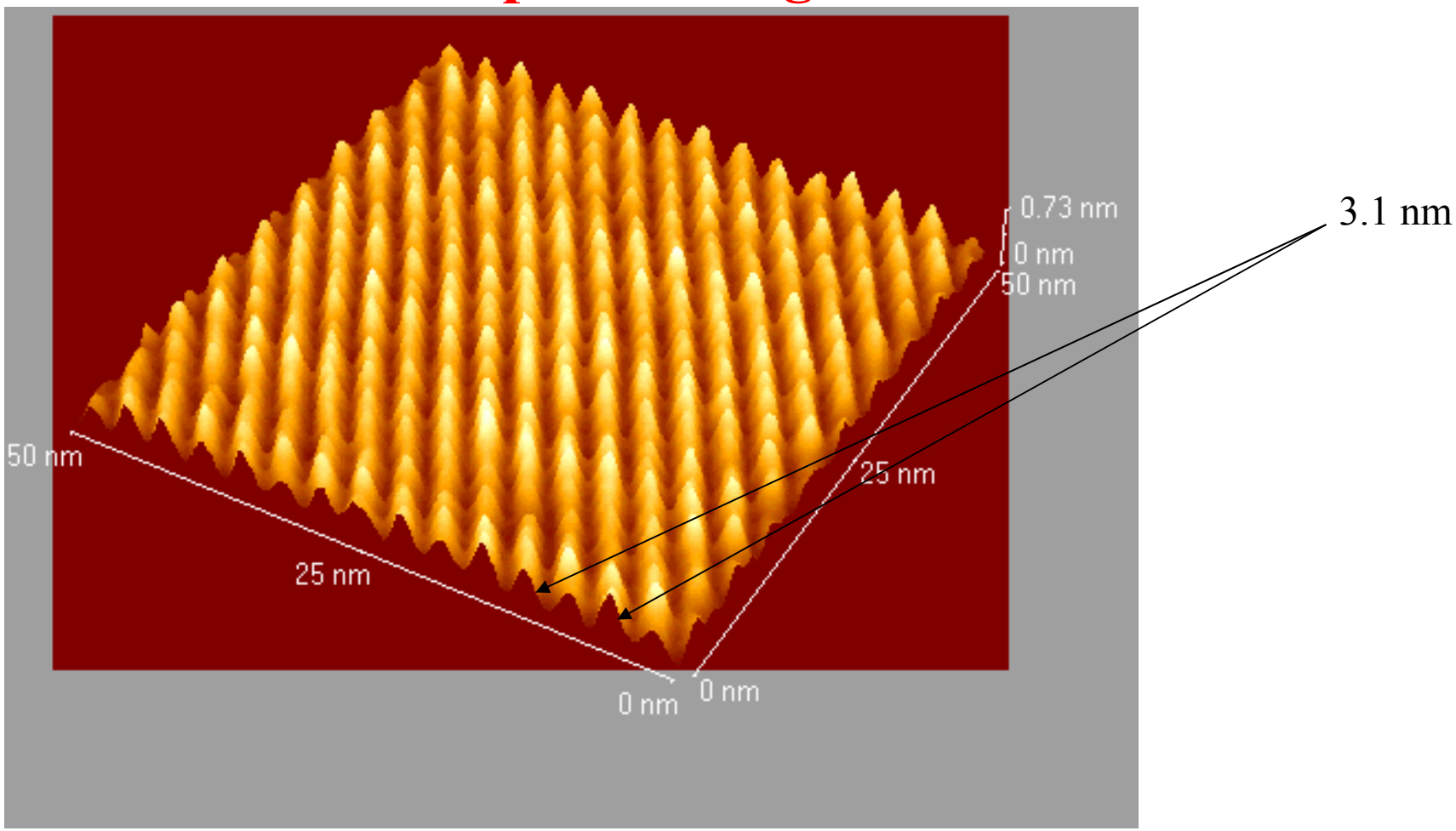


^{29}Si Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample

87 % condensation of the organosilicate precursor was observed



AFM Topography of Phenylene-Bridged Nanoporous Organosilicate



Instrument: Thermomicroscopes AutoProbe CP Research Scanning Probe Microscope (SPM)
Scan mode: Non-contact mode in air at a rate of 500nm/s.
Canilever: Gold coated V-shaped silicon nitride cantilever with resonant frequency =117.08 kHz. and spring constant of 0.5 N/m. Tip radius= 10 nm

Summary

- Successful synthesis of zeolite Y nanoparticles in the presence of organics to < 100 nm, but further reduction in particle size needed.

- Successful synthesis of a wide range of silicate, aluniosilicate, and organosilicate nanoporous hosts up 3+ nm, but further expansion of pore diameter needed.

Summary of Organosilicate Synthesis

A.

- High surface area nanoporous phenylene-briged organosilicate was synthesized by acid catalyzed hydrolysis and condensation in the presence of 1,4 bis-triethoxysily benzene and non-ionic oligomeric surfactant Brij 76 ($C_{18}H_{35}$ $(OCH_2CH_2)_{10}OH$) as template.

- Material has pore diameter of 27.4 Å, pore volume 0.46 cm^3/g, and surface area of 784 m^2/g.

- Approximately 67 % condensation of the precursor was achieved.

B. High surface area nanoporous phenylene-briged organosilicate was also synthesized by base catalyzed hydrolysis and condensation in the presence of 1,4 bis-triethoxysily benzene and catonic surfactant ($C_{16}H_{33}N(CH_3)_3Br$ as template.

- Material has pore diameter of 31 Å, and pore volume of 0.58 cm^3/g, and surface area of 876 m^2/g.

- Approximately 80 % of the precursor was achieved.

Future Work

- Continue to explore synthesis variables to reduce the size of the nanocrystals
- Expand the pore dimension of nanoporous hosts from 4 nm towards 30 nm using pore size expanders e.g. trimethylbenzene
- Insert zeolite Y nanocrystals in nanoporous materials
- Catalysts testing.

Acknowledgements

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Personnel

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- Taurean Hodges - Undergraduate Student (Chemistry)
- Ifedapo Adeniyi - Undergraduate (Engineering)